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STUDY OF BARRIER PROPERTIES OF POLYMERIC FILMS TO VARIOUS ORGANIC AROMATIC VAPORS

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I. INTRODUCTION

The proper selection of a flexible material for food packaging is essential in order to provide barrier properties against pick-up by transmission of unfavorable organic compounds from the atmosphere as well as oxygen and water. On the other hand, a good barrier is needed in order to retain the aroma and flavor of the product; to afford a proper shelf-life.

The mechanism of transmission of gases and vapors through polymeric membranes is either by leakage or permeation (Barrer, 1951). Leakage occurs when there is a discontinuity in the material. This discontinuity may be due to a pinhole, a crack, a faulty seal, etc. Permeation through the barrier is characterized by condensation on the entering surface, followed by solution in the film, diffusion through it and evaporation on the low concentration side (Hall, 1973).

The type of permeant, the structure of the plastic film as well as environmental conditions affect the rate of permeation. These include: nature of permeating molecule, its size and shape; nature of the barrier material and its structure - degree of crosslinking and crystallinity and the molecular orientation. Other parameters are the concentration gradient, thickness of the laminate and its area, temperature, relative humidity.

Permeability of polymeric films to various organic vapors was reported by Simril and Hershberger (1950). These authors found that the presence of bulky side chains and the introduction of plasticizers increased permeability to various vapors.

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Lebovits (1966) reviewed the state of the art of permeability and polymers up to this date.

Niebergall et al. (1978) developed a measuring apparatus with the aid of which aroma-permeation of packaging foils is possible at all conditions.

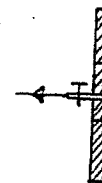
In this work the permeability of various polymeric films to various volatiles, noxious as well as food destined ones at very low concentration was investigated. This was done in order to simulate conditions in a supermarket where food products are in proximity with nonfood items, and very low concentration are affecting the sensory quality of the food.

II. METHOD

Permeabilities were determined by the Gilbert-Pegaz permeation cell method (Gilbert and Pegaz, 1969).

The cell (Fig. 1) used, accommodates simultaneously two samples of films, thus doubling the exposure area. A pair of films is clamped between the parts of the cell and nitrogen is flushed through the upper and lower sections of the cell to remove any traces of air. To maintain a constant driving force on one side of the film nitrogen is flushed through the volatile component, tested and carried through the middle section throughout the test. The permeation through the two films is evaluated by periodical sampling of the volatile concentration on both the upper and lower compartments of the permeation cell.

In some cases like in menthol permeation, the compound was put in solid form in the lower compartment of the cell in a small aluminum cap separated from the upper compartment by the film under test. The volatiles' concentrations were determined using a Hewlett-Packard 5750 Gas Chromatograph with dual flame ionization detectors. Separation was done on an aluminum column (6' x $\frac{1}{8}$ ") with 10% SE 30 on 80/100 Supelcoport (Supelco, Inc.). The carrier gas was nitrogen at a flow rate of 40 ml/min. The GC conditions were as follows: detector temperature was 240°C and injector part 230°C. The column was operated isothermally and its temperature was varied according to the boiling point of the volatile tested. Samples of 0.5 ml from the top and bottom compartment were injected periodically for permeation determination. The sample from the middle section was used for determination of the driving force. The peak area was determined by a Varian CDS-111 integrator.



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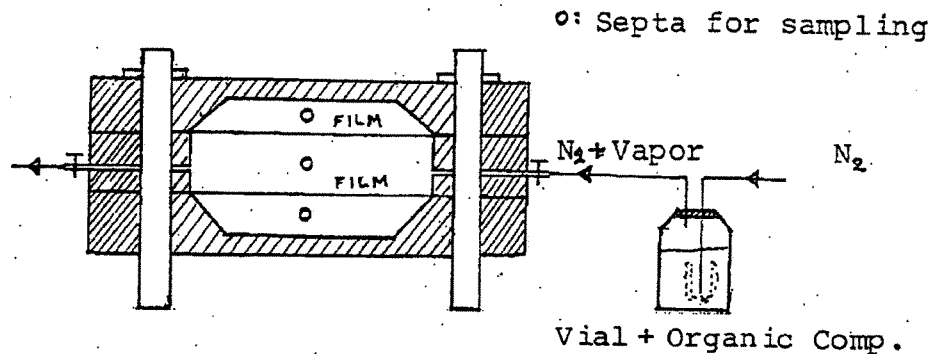
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FIGURE 1. Permeation Cell Used For The Experiments.

III. MATERIALS

The materials and volatiles tested in this work are listed in Table 1.

The films were tested as flat sheets and also their flex resistance was tested according to ASTM method F-392-74. The films were partial flexed for 20 cycles (condition E) with a Gelbo Flex Tester (U.S. Testing Inc.)

The volatiles used were: toluene, ethyl acetate, methyl ethyl ketone - as the industrial indirect additives and orange oil and menthol as food flavors. For each volatile a calibration curve was constructed.

IV. RESULTS AND DISCUSSION

Table 1 shows the results of permeability constants of the various films to the volatile organic materials.

The permeation rate is expressed as grams of the volatile penetrating through 1 m² on the tested plastic material,

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during 24 hours, under a concentration gradient of 100 ppb of the volatile tested. This low concentration was chosen to simulate conditions existing in the retail stores where food products are in close proximity with detergents and solvents. Also the threshold values of various food flavors as well as non-foods volatiles are within this range of concentration.

Glassine and the nylon coextrusion (No. 1, 5 on Table 1) have better barrier properties against volatile permeation as compared to the other materials tested. But when flexed, many pinholes appeared in the glassine, noted even by a naked eye as held under a light source. The nylon coextrusion on the other hand was only wrinkled, and no pinholes could be observed, as is shown in the data.

The polypropylene (No. 2) did not provide a good barrier to all the volatiles tested. Also the pp/pp coated with PVDC (No. 4) did not provide a good barrier and had the highest permeation rate for most permeants.

Regarding the rate of permeation. Two types of permeation were observed from the flexed films. One showed a normal pattern where there is a lag phase followed by a steady state. (Figure 2).

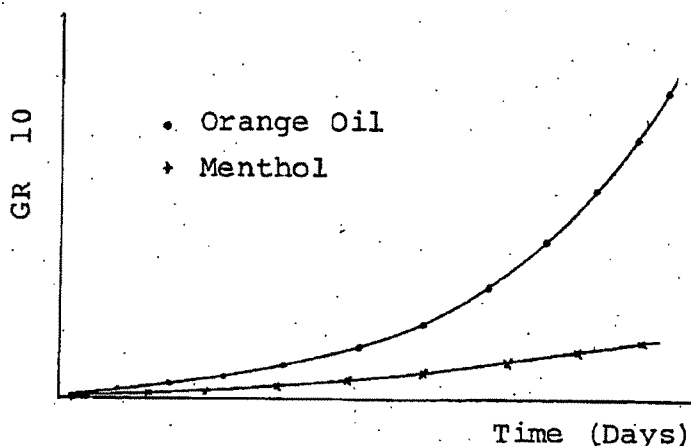


FIGURE 2. Typical Permeation Curves

This behavior was typical of the high boiling point volatiles, namely the orange oil and the menthol. The lag phase in all films was a couple of weeks. In the nylon/PE

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extrusion and the PP/PE coated with PVDC proved to be the best barriers, indicating the potential of these materials to protect the product from loss of aroma and flavor to enable a proper shelf-life.

The second type showed initial rapid increase in permeation and then a constant decreased rate of change. (Figure 3)

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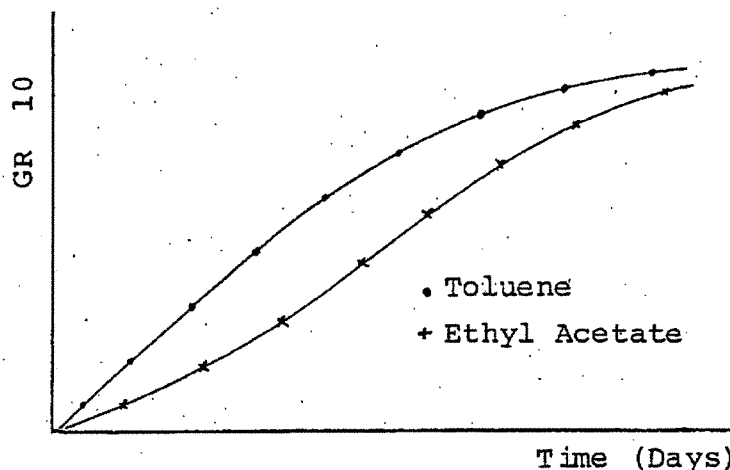


FIGURE 3. Typical Permeation Curves

This behavior was typical to PP/PE - PVDC coated for both the low boiling solvents toluene and ethyl acetate. This type of permeation may be less desirable for odor barrier since concentration dependence of the permeability coefficient is exhibited in contrast to the lag time/linear coefficients of the nylon containing composites. In the case of nylon these hydrophobic solvents do not swell the base polymer since hydrophobic bonds are responsible for intermolecular bonding forces.

In the case flexed Glassine the extremely high values in Table I are attributed to presence of pinholes in the film which sharply increase the permeation rate.

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TABLE I. Permeability Constants of Various Polymers to Organic Flavors.^a

Film	Thickness mil	Toluene		Ethyl acetate		MEK		Orange		Menthol	
		U	F	U	F	U	F	U	F	U	F
1. Glassine	1.5	0.028	0.142	<0.012	0.676	<0.088	0.145	<0.025	0.150	<0.148	0.040
		30.190*			148*		157*				
2. Polypropylene	-	3.000*	-	2.56	-	-	-	-	0.440	-	0.320
3. PP/PE + PVDC	1.8	0.550	1.820*	0.790	10.030	0.370	0.250	<0.020	0.010	<0.008	<0.020
4. PP/PP + PVDC	1.8	0.580	0.920	0.760	1.720	0.230	0.830	0.570	0.930	0.900	1.090
5. PE/NYLON/PE	1.5	0.069	0.034	<0.011	<0.011	<0.082	<0.022	<0.020	0.002	<0.116	<0.010

^aUnits are in gr/24hr · m² · 100 ppm.

*These films have sharply increased rate of permeation.

U - flat unflexed sheet

F - after flexing

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The case of higher permeability values of unflexed films than flexed ones, as clearly is observed in Table I for PE/NYLON/PE, is attributed to orientation of polymer chains on flexing with consequent increase in "packing" of these macromolecules.

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